



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of

BRUNNER

Serial No. 09/879,456

Filed: June 13, 2001

For: HYDROGENATION OF BENZENEPOLYCARBOXYLIC ACIDS OR
DERIVATIVES THEREOF USING A CATALYST CONTAINING MACROPORES

DECLARATION

I, Boris B. Breitscheidel, state as follows:

I received a M. Sc. ("Dipl.-Chem.") and a Ph. D. in Chemistry from the University of Würzburg, Germany.

In 1991, I started working for BASF AG, Ludwigshafen, Germany, as a research scientist with a special focus on catalysts and catalytic reactions. Since 1998, I am working in the plasticizer department of BASF AG, Ludwigshafen, Germany, dealing with product development and technical marketing of plasticizers. So far, I have filed more than 20 patent applications in the field of plasticizers.

Based on my education and my professional activities, I am experienced in product development and testing of plasticizers for new applications.

I am a co-inventor of the above-referenced application and have read the Office action of February 27, 2004, and August 25, 2004.

In order to demonstrate the nonobviousness of the invention claimed therein, we have conducted the following comparative examples.

Starting from commercially available n-nonanol (Acros Organics, order no. 15747-2500) or commercially available n-decanol (Acros Organics, order no. 16576-0025), respectively, di-n-nonylphthalat or di-n-decylphthalat were prepared by esterification with phthalic acid anhydride. These phthalates with linear alkyl residues were then hydrogenated according to the process described in application 09/879,456 to the respective di-n-nonylcyclohexanedicarboxylate or di-n-decylcyclohexanedicarboxylate. Subsequently, these cyclohexanedicarboxylates with linear alkyl residues were tested in view of their properties as plasticizers for PVC in different applications and compared to the corresponding plasticizers according to the invention of application 09/879,456, i. e. with diisononylcyclohexanedicarboxylate of Example 2 or Example 14, respectively, and diisodecylcyclohexanedicarboxylate prepared according to Example 2, in their properties as plasticizers.

Furthermore, the properties of the plasticizers according to the invention of application 09/879,456 at low temperatures were compared to those of the known plasticizer di-(2-ethylhexyl)-cyclohexane-1,2-dicarboxylate (according to DE-A 126 32 96).

Description of the tests:

Plasticizers:

- 1) di-n-nonylcyclohexanedicarboxylate (prepared as described above)
- 2) di-n-decylcyclohexanedicarboxylate (prepared as described above)
- 3) diisononylcyclohexanedicarboxylate according to Example 2 or 14 of application 09/879,456
- 4) diisodecylcyclohexanedicarboxylate analogous Example 2 of application 09/879,456
- 5) di-(2-ethylhexyl)-cyclohexane-1,2-dicarboxylate (according to DE-A 126 32 96)

Tests of the Plasticizer:

For the pure plasticizer 1 to 4, the solution temperature at the clear point for PVC was measured (according DIN 53408). The solution temperature at the clear point is a measure for the gelation performance of a plasticizer. The higher the solution temperature at the clear point, the lower is the gelation performance.

Preparation of soft-PVC-compounds (test sample):

In each case, 100 parts suspension PVC (K-value 71, type "Vinoflex S 7114" or "Solvin 271 SP"), 67 parts of plasticizer and 2 parts Ba/Zn-stabilizer (type "Lankromark LZB 753") were mixed with a hand-mixer at room temperature. The mixture was then plastified on a steam-heated laboratory rolling mill (company Collin, type "150") and processed to a sheeted-out compound. The temperature of both cylinders was 170 to 180 °C, the turn number was about 15 turns per minute (front roll) and 12 turns per minute (back roll); the milling time was 5 minutes. A sheeted-out compound was obtained with a thickness of 0.55 mm. The cooled sheeted-out compound was afterwards molded on a press of the type "400 P" of company Collin at a temperature of 180 to 190 °C and a pressure of 220 bar within 400 seconds to a soft-PVC-film with a thickness of 0.50 mm.

Testing of the soft-PVC-compounds:

For the soft-PVC-films, the mechanical properties (tensile strength according to DIN 53455 or DIN EN ISO 527, part 1 and 3), the thermostability (thermostability according to DIN 53381, part 2, process E, and HCl thermal stability according to VDE-norm 0472, §614), and the compatibility (according to BASF-method as described below) were tested.

All results of the tests are listed in the following two tables. In each case the cyclohexanedicarboxylate according to the invention with a branched alkyl residue is compared to the corresponding cyclohexanedicarboxylate with a linear alkyl residue.

Parameter	Testing Method	<u>Plasticizer</u>	
		Diisononylcyclohexanedicarboxylate according to Example 2 or 14 of 09/879,456	Di-n-nonylcyclohexanedicarboxylate
Solution temperature at the clear point for PVC (°C)	DIN 53408	150	154
Tensile Strength (N/mm ²)	DIN 53447	17.6	16.4
Thermostability at 180 °C (min)	DIN 53381, Part 2, Process E	127	116
HCl thermal stability at 200 °C (min)	VDE-Norm 0472, §614	21.0	19.8
Compatibility (Weight Loss after 7 days (%))	BASF-Method (as described below)	0.47	0.57

Parameter	Testing Method	<u>Plasticizer</u>	
		Diisodecylcyclohexanedicarboxylate analogous to Example 2 of 09/879,456	Di-n-decylcyclohexanedicarboxylate
Solution temperature at the clear point for PVC (°C)	DIN 53408	160	164
Tensile Strength (N/mm ²)	DIN 53447	19.1	16.4
Thermostability at 180 °C (min)	DIN 53381, Part 2, Process E	127	118
HCl thermal stability at 200 °C (min)	VDE-Norm 0472, §614	21.7	19.8
Compatibility (Weight Loss after 7 days (%))	BASF-Method (as described below)	0.41	0.87

Both comparisons show that the solution temperature at the clear point of the cyclohexanedicarboxylates with branched alkyl residues according to the invention is significantly lower than the solution temperature at the clear point of the corresponding cyclohexanedicarboxylates with a linear alkyl residue. Therefore, the gelation performance of the plasticizers according to the invention is better.

Above this, the tensile strength of the soft-PVC-compounds prepared using the cyclohexanedicarboxylates with branched alkyl residues according to the invention is higher than that of those prepared from the corresponding cyclohexanedicarboxylates with a linear alkyl residue. The plasticizers according to the invention therefore lead to better mechanical properties.

Furthermore, the thermostability and the HCl thermal stability of the soft-PVC-compound prepared using the cyclohexanedicarboxylates with branched alkyl residues according to the invention are significantly higher than those of the ones prepared from the corresponding cyclohexanedicarboxylates with a linear alkyl residue. The plasticizer according to the invention therefore leads to better thermostability.

Additionally, the cyclohexanedicarboxylates with branched alkyl residues according to the invention show better compatibility with PVC (lower loss in weight) than the corresponding cyclohexanedicarboxylates with linear alkyl residues.

Thus, the comparative examples show that the cyclohexanedicarboxylates according to the invention surprisingly show advantageous properties as plasticizers which can be put down to the branched alkyl residues.

Furthermore, plasticizers 3 and 4 according to the invention of application 09/879,456 were compared to di-(2-ethylhexyl)-cyclohexane-1,2-dicarboxylate regarding the low temperature flexibility of plastics prepared using cyclohexane dicarboxylic acid esters as plasticizer. The flexibility at low temperature of plastics is characterized by the break at low temperature and the stiffness in torsion. The lower the break at low temperature and the stiffness in torsion, the better is the flexibility at low temperature of the plastic.

The soft-PVC-compounds were prepared as described above.

Testing of the soft-PVC-compounds:

For the soft-PVC-films, the break at low temperature and the stiffness in torsion were measured according to DIN 53372 and DIN 53447. The results are given in the following table.

Plasticizer	Break at low temperature (according to DIN 53372)	Stiffness in torsion (according to DIN 53447)
Di-(2-ethylhexyl)-cyclohexane-1,2-dicarboxylate	-37.5	-37
Diisononylcyclohexane-1,2-dicarboxylate	-41.7	-44
Diisodecylcyclohexane-1,2-dicarboxylate	-37.5	-42

The results show that diisononylcyclohexane-1,2-dicarboxylate according to the invention of application 09/879,456 has an especially low break at low temperature and stiffness in torsion in comparison to di-(2-ethylhexyl)-cyclohexane-1,2-dicarboxylate according to DE-A 126 32 96 and diisodecylcyclohexane-1,2-dicarboxylate.

Description of the BASF-Method for Testing of Compatibility of Plasticizers

The compatibility of a plasticizer in a soft-PVC-compound is determined by measuring the loss in weight of a soft-PVC-compound due to exudation of the plasticizer after a defined time by weighing the compound after the soft-PVC-compound was stored at a temperature of 70 °C and 100 % relative humidity over a longer period. The determination of the compatibility is carried out according to the following description:

Purpose of the Testing

The testing is done for the quantitative measurement of the compatibility of plasticizers in soft-PVC-mixtures. It is carried out at elevated temperature (70 °C) and humidity (100 % relative humidity). The data obtained are analyzed in comparison to the storage time.

Testing Sample

For the testing, testing samples (films) with a size of 75 x 110 x 0.5 mm are used. A hole is punched in the longer side of the films, the film is marked (soldering bit) and weighed.

Testing Apparatus

Heraeus-heating oven at 70 °C, analysis scale, temperature measuring apparatus
Testotherm with sensor for measuring within the heating oven.

Description

The temperature within the heating oven is set to 70 °C. The previously prepared weighed films are hung up on a wire which is fixed in a glass bowl which is filled to about 5 cm with water (VE-water). The films should not touch each other. The lower edges of the films must not hang in the water. The glass bowl is sealed with a PE-film

to avoid leaking of the steam which is prepared within the glass bowl. The water level in this glass bowl is checked daily and after water loss additionally water is added.

Storage Time

Each day, two films are taken from the glass bowl and climatized for one hour in air. Afterwards, the films are cleaned at the surface with methanol. Then, the films are dried for 16 hours at 70 °C in a drying oven with forced convection hanging free. After removal from the drying oven, the films are climatized for one hour hanging free and then weighed. In each case the average value is given for the loss of weight of the films.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Boris B. Breitscheidel
Boris B. Breitscheidel, Ph.D.

Date: 15.10.2004

No guarantee can be given in respect of this translation

In all cases the latest German-language version of this standard shall be taken as authoritative

Testing of Plastics
Determination of Solubility Temperature
of Polyvinyl Chloride (PVC) in Plasticizers

DIN

53408

Prüfung von Kunststoffen;
Bestimmung der Lösetemperatur von Polyvinylchlorid (PVC) in Weichmachern

1. Purpose and application

The object of the testing specified in this Standard is to determine the temperature at which a given polyvinyl chloride (PVC) is clearly soluble in plasticizers¹⁾. Conversely, this method can also be used if various polyvinyl chlorides are to be examined with regard to a given plasticizer. This solubility temperature of polyvinyl chloride (PVC) in plasticizers (see Section 2) is closely related to the gelling properties of a plasticizer for PVC. Knowledge of this temperature is therefore of importance in judging various plasticizers with regard to their dissolving power for a given type of polyvinyl chloride.

2. Definition

Under this Standard the solubility temperature is the temperature at which a plasticizer completely dissolves a given polyvinyl chloride.

3. Sampling

An average specimen of both the plasticizer and polyvinyl chloride should be taken, sufficient for 3 testings.

4. Number of testings

3 specimens are tested with each plasticizer. If the individual readings obtained for the solubility temperature differ by more than 1.5 deg from the mean value the testing must be repeated.

5. Test apparatus and test media

Balance with a margin of error of ± 0.005 g
Thermometer scaled at intervals of 1 deg
50 ml beaker (e.g. tall beaker 50 with pouring lip DIN 12331)
Glass rod, 3 mm diameter
Microscope slide with cover glasses (e.g. according to DIN 58884, at present circulating as draft)
Microscope giving 100 x magnification
Heated microscope stage²⁾

Note: When using a heated microscope stage previous control of the instrument and of the relevant thermometer is necessary by determining the melting points of so-called "calibration salts".

Polyvinyl chloride (in powder form)

6. Procedure

- 6.1. Weigh in 1 g polyvinyl chloride and 19 g plasticizer, both to the nearest 0.01 g, and mix until a homogeneous slurry is obtained. Use the glass rod to apply a drop of this slurry to the middle of the slide and cover with a glass.
- 6.2. Heat the microscope stage to 60 °C. Then place the prepared specimen on the microscope stage so that it can be studied in transmitted light.
- 6.3. Adjust the heating of the microscope stage so that the temperature rises at a rate of 2 deg per minute.
- 6.4. The solubility temperature is taken as being the temperature at which the final particles of PVC become invisible as a result of the dissolving process and the specimen reveals no further outlines or contrasts under the microscope.

7. Test report

The test report should make reference to this Standard and include the following particulars:

- Type and designation of plasticizer
- Type and designation of polyvinyl chloride
- Number of testings
- Solubility temperature, mean value rounded to 1 deg
- Date of test

¹⁾ see DIN 55945 Sheet 1 for definition of plasticizer.

²⁾ Committee for Plastics in the DINA, 1 Berlin 30, Burggrafenstrasse 4-7, provides sources of supply on request.

Explanations on page 2

Explanations

This Standard was drawn up by the joint Advisory Committee 13 for "Plastic Auxiliaries (plasticizers)" of the Committees for Plastics and Surface Coatings in the German Standards Institution (DNA).

The stated test method is chiefly intended to characterize plasticizers according to their dissolving power for polyvinyl chloride (PVC). For this purpose it is necessary to use the same PVC for all testings. If the testing is carried out at various laboratories it is advisable to exchange the PVC used for the examinations.

The method can also be used to determine differences in the solubility of various types of PVC (dependence of solubility on manufacturing process, emulsion PVC, suspension PVC, copolymers etc.). A definite plasticizer should be fixed for comparative examinations.

Some practice is necessary for carrying out the testing as disappearance of the grains may take some time and an optically clear solution is not obtained. The method merely permits comparative investigations and does not yield any absolute characteristic values.

Annex A (informative)

Young's modulus and related values

Due to their viscoelastic behaviour many properties of polymer materials depend not only on temperature but also on time. With regard to the tensile test, this causes nonlinear stress/strain curves (bending towards the strain axis) even within the range of linear viscoelasticity. This effect is pronounced in the case of tough polymers. Consequently, the values of the tangent modulus of tough materials taken from the initial part of the stress/strain curves often depend strongly on the scales used. Thus the conventional method (tangent at the initial point of the stress/strain curve) does not give reliable moduli for these materials.

The method for the measurement of Young's modulus prescribed in this part of ISO 527 is based, therefore, on two specified strain values, i.e. 0,25 % and 0,05 %. (The lower strain value has been set at not zero in order to avoid errors in the measured modulus

caused by possible onset effects at the beginning of the stress/strain curve.)

In the case of brittle polymers, both the new and the conventional methods give the same values for the modulus. The new method, however, allows accurate and reproducible measurement of the moduli of tough plastics. The definition of the initial tangent modulus, therefore, has been deleted in the present part of ISO 527.

The aspects mentioned above for the modulus similarly relate to the "offset yield point", which in ISO/R 527 was defined by the deviation of the stress/strain curve from its initial linearity. The offset yield point, therefore, is replaced by a point of specified strain (stress at x % strain, σ_x , see 4.3.4). Since the definition of such a "substitute" yield point is significant for tough materials only, the specified strain shall be chosen near the yield strain commonly found.

	Plastics – Determination of tensile properties Part 3: Test conditions for films and sheets (ISO 527-3 : 1995 + Corr 1 : 1998 + Corr 2 : 2001) (includes Corrigendum AC : 1998 + AC : 2002) English version of DIN EN ISO 527-3 : 1995 + AC : 1998 + AC : 2002	DIN EN ISO 527-3
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ICS 83.140

Supersedes October 1995 edition.

Kunststoffe – Bestimmung der Zugeigenschaften – Teil 3: Prüfbedingungen für Folien und Tafeln
 (ISO 527-3 : 1995 + Corr 1 : 1998 + Corr 2 : 2001)
 (enthält Berichtigung AC : 1998 + AC : 2002)

European Standard EN ISO 527-3 : 1995 + Corrigendum AC : 1998 + AC : 2002 has the status of a DIN Standard.

A comma is used as the decimal marker.

National foreword

This standard has been published in accordance with a decision taken by CEN/TC 249 to adopt, without alteration, International Standard ISO 527-3 as a European Standard.

The responsible German body involved in its preparation was the *Normenausschuss Kunststoffe* (Plastics Standards Committee), Technical Committee *Kunststoff-Folien und kunststoffbeschichtete Flächengebilde (Kunstleder); allgemeine Eigenschaften*.

DIN EN ISO 527-1 and DIN 53360 are the standards corresponding to International Standards ISO 527-1 and ISO 4593, respectively, referred to in clause 2 of the EN.

Amendments

This standard differs from the October 1995 edition in that some corrections have been made in figures 3 and 4.

Previous editions

DIN 53371: 1955-10, 1959-09; DIN 53455: 1952-10, 1968-04, 1981-08; DIN EN ISO 527-3: 1995-10; DIN EN ISO 527-3 Corr 1: 1998-09.

National Annex NA

Standards referred to

(and not included in **Normative references**)

- | | |
|------------------|---|
| DIN 53370 | Determination of plastic film and sheeting thickness by mechanical scanning |
| DIN EN ISO 527-1 | Plastics – Determination of tensile properties – Part 1: General principles
(ISO 527-1 : 1993 + Corr 1 : 1994) |

EN comprises 6 pages.

English version

Plastics – Determination of tensile properties

Part 3: Test conditions for films and sheets

(ISO 527-3 : 1995 + Corr 1 : 1998 + Corr 2 : 2001)

(includes Corrigendum AC : 1998 + AC : 2002)

Plastiques – Détermination des propriétés en traction – Partie 3: Conditions d'essai pour films et feuilles
(ISO 527-3 : 1995 + Corr 1 : 1998 + Corr 2 : 2001) (corrigendum AC : 1998 + AC : 2002 inclut)

Kunststoffe – Bestimmung der Zug-eigenschaften – Teil 3: Prüfbedingungen für Folien und Tafeln
(ISO 527-3 : 1995 + Corr 1 : 1998 + Corr 2 : 2001) (enthält Berichtigung AC : 1998 + AC : 2002)

This European Standard was approved by CEN on 1995-07-29, corrigendum AC : 1998 on 1998-06-18 and corrigendum AC : 2002 on 2002-07-24.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

The European Standards exist in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, the Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, the Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom.

CEN

European Committee for Standardization

Comité Européen de Normalisation

Europäisches Komitee für Normung

Management Centre: rue de Stassart 36, B-1050 Brussels

Foreword

International Standard

ISO 527-3 : 1995 Plastics – Determination of tensile properties – Part 3: Test conditions for films and sheets, which was prepared by ISO/TC 61 'Plastics' of the International Organization for Standardization, has been adopted by Technical Committee CEN/TC 249 'Plastics' as a European Standard.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, and conflicting national standards withdrawn, by February 1996 at the latest.

In accordance with the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard:

Austria, Belgium, the Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, the Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom.

Endorsement notice

The text of the International Standard ISO 527-3 : 1995 was approved by CEN as a European Standard without any modification.

1 Scope

1.1 This part of ISO 527 specifies the conditions for determining the tensile properties of plastic films or sheets less than 1 mm thick, based upon the general principles given in part 1.

NOTE 1 For sheets greater than 1 mm thick, the user is referred to part 2 of this International Standard.

1.2 See ISO 527-1, subclause 1.2.

1.3 This part of ISO 527 is not normally suitable for determining the tensile properties of:

- a) cellular materials;
- b) plastics reinforced by textile fibres.

1.4 See ISO 527-1, subclause 1.5.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 527. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 527 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO

maintain registers of currently valid International Standards.

ISO 527-1:1993, *Plastics — Determination of tensile properties — Part 1: General principles*.

ISO 4591:1992, *Plastics — Film and sheeting — Determination of average thickness of a sample, and average thickness and yield of a roll, by gravimetric techniques (gravimetric thickness)*.

ISO 4593:1993, *Plastics — Film and sheeting — Determination of thickness by mechanical scanning*.

3 Principle

See ISO 527-1, clause 3.

4 Definitions

See ISO 527-1, clause 4.

5 Apparatus

See ISO 527-1, clause 5, subject to the following additional requirements:

In 5.1.2, the tensile-testing machine shall be capable of maintaining the speeds of testing as specified in table 1 of ISO 527-1. It is normal for films and sheets to be tested at a speed of 5 mm/min, 50 mm/min, 100 mm/min, 200 mm/min, 300 mm/min or 500 mm/min. The information contained in ISO 527-1, subclause 9.6, also applies.

In 5.1.5, when testing thin sheets or film material, the specimen shall not carry the weight of the extensometer.

In 5.2, devices complying with the requirements in ISO 4593 shall be used for measuring the thickness, except in the case of very thin film (less than 0.01 mm thick) or embossed film. In those cases, the thickness shall be determined by the method specified in ISO 4591. When ISO 4591 is used, the average thickness of the film sample shall be taken as the thickness of the test specimen.

6 Test specimens

6.1 Shape and dimensions

6.1.1 The preferred form of test specimen for the determination of tensile properties by this method is a strip 10 mm to 25 mm wide and not less than 150 mm long (specimen type 2 — see figure 1),

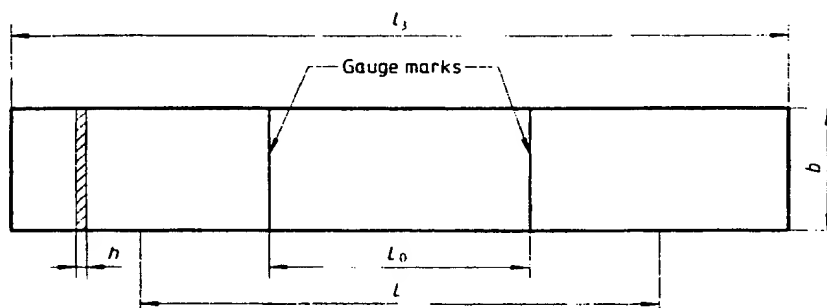
having two parallel gauge marks, 50 mm apart, on the central portion of the specimen.

Some film materials have a very high elongation at break which may result in them being outside the stretching capacity of the testing machine. In such cases, it is permissible to reduce the initial distance between the grips to 50 mm.

6.1.2 When required by the specification for the material under test or for routine quality-control tests, dumb-bell specimen types 5, 1B and 4 of the shape and dimensions shown in figures 2, 3 and 4 may be used. These specimens are convenient to produce and permit rapid quality-control testing.

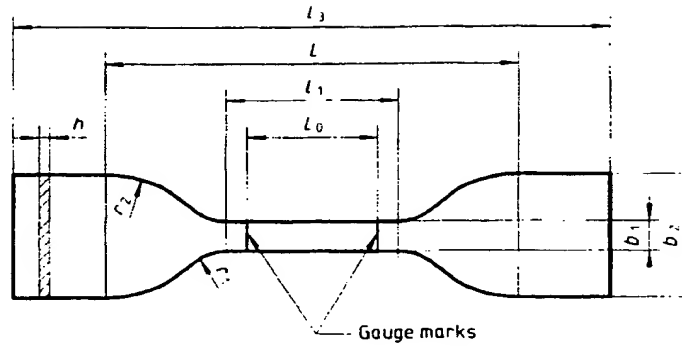
Specimen type 5 (figure 2) is recommended for film and sheet with a very high strain at break. Specimen type 4 is recommended for other types of flexible thermoplastic sheet.

Specimen type 1B (figure 3) is recommended for rigid sheets.



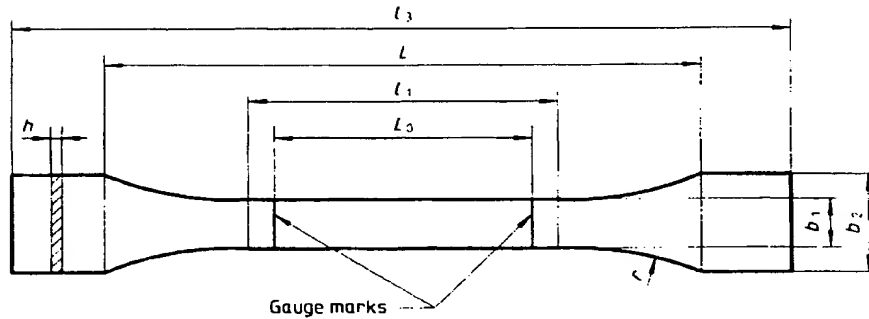
- b Width: 10 mm to 25 mm
- h Thickness: ≤ 1 mm
- L_0 Gauge length: $50 \text{ mm} \pm 0.5 \text{ mm}$
- L Initial distance between grips: $100 \text{ mm} \pm 5 \text{ mm}$
- l_3 Overall length: $\geq 150 \text{ mm}$

Figure 1 — Specimen type 2



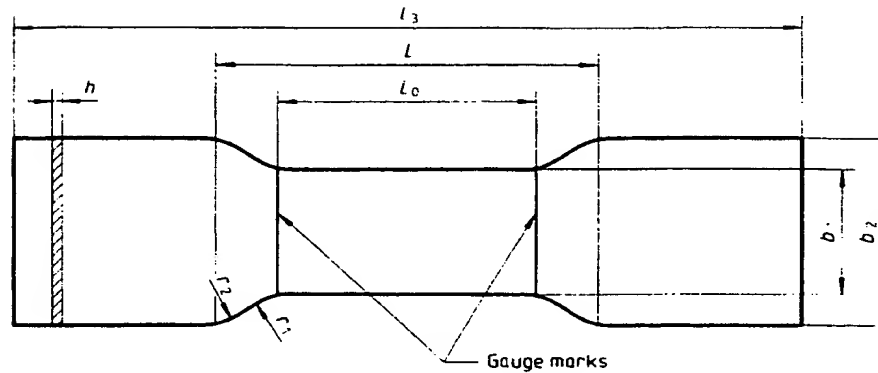
- b_1 Width of narrow parallel-sided portion: 6 mm \pm 0,4 mm
- b_2 Width at ends: 25 mm \pm 1 mm
- h Thickness: \leq 1 mm
- L_0 Gauge length: 25 mm \pm 0,25 mm
- l_1 Length of narrow parallel-sided portion: 33 mm \pm 2 mm
- L Initial distance between grips: 80 mm \pm 5 mm
- l_3 Overall length: \geq 115 mm
- r_1 Small radius: 14 mm \pm 1 mm
- r_2 Large radius: 25 mm \pm 2 mm

Figure 2 — Specimen type 5



- b_1 Width of narrow parallel-sided portion: 10 mm \pm 0,2 mm
- b_2 Width at ends: 20 mm \pm 0,5 mm
- h Thickness: \leq 1 mm
- L_0 Gauge length: 50 mm \pm 0,5 mm
- l_1 Length of narrow parallel-sided portion: 60 mm \pm 0,5 mm
- L Initial distance between grips: 115 mm \pm 5 mm
- l_3 Overall length: \geq 150 mm
- r Radius: \geq 60 mm (recommended radius: 60 mm \pm 0,5 mm)

Figure 3 — Specimen type 1B



b_1	Width of narrow parallel-sided portion: 25,4 mm \pm 0,1 mm
b_2	Width at ends: 38 mm
h	Thickness: \leq 1 mm
L_0	Gauge length: 50 mm \pm 0,5 mm
L	Initial distance between grips: 98 mm
l_3	Overall length: 152 mm
r_1	Small radius: 22 mm
r_2	Large radius: 25,4 mm

Figure 4 — Specimen type 4

6.2 Preparation of specimens

6.2.1 The test specimens described in 6.1.1 shall be cut or punched so that the edges are smooth and free from notches; examination with a low-power magnifier is recommended to check the absence of notches. Razor blades, suitable paper cutters, scalpels or other devices capable of cutting the specimens to the proper width and producing straight, clean, parallel edges with no visible imperfections shall be used. Punch dies shall be kept sharp by regular honing, and a suitable backing material shall be used with punch dies to ensure a clean-cut edge.

6.2.2 The test specimens described in 6.1.2 shall be obtained by the use of punch dies, using suitable backing material to ensure a clean-cut edge. Dies shall be kept sharp by regular honing, and the edges of the specimen shall be examined with a low-power magnifier to ensure the absence of notches. Discard any specimen with obvious imperfections on the cut edges.

6.3 Gauge marks

See ISO 527-1, subclause 6.3.

The marking device used to produce the gauge marks shall have two parallel edges which are ground smooth and true, 0,05 mm to 0,10 mm wide at the edge and bevelled at an angle of not more than 15°. An ink stamp may also be used to apply ink to the area of the gauge marks, before or after producing them with the marking device, using an ink of a suitable contrasting colour that has no deleterious effect on the film being tested.

6.4 Checking the specimens

Discard any test specimen with obvious imperfections on the cut edges.

6.5 Anisotropy

The properties of certain types of film material may vary with direction in the plane of the film (anisotropy). In such cases, it is essential to prepare two groups

of test specimens with their major axes respectively parallel and perpendicular to the direction of orientation of the film.

7 Number of specimens

See ISO 527-1, clause 7.

8 Conditioning

See ISO 527-1, clause 8.

9 Procedure

See ISO 527-1, clause 9.

10 Calculation and expression of results

See ISO 527-1, clause 10, except for "10.3 Modulus calculation", and "10.4 Poisson's ratio, μ ".

11 Precision

The precision of the test method is not known because inter-laboratory data are not available. When inter-laboratory data are obtained, a precision statement will be added at the following revision.

12 Test report

The test report shall include the following information:

- a) a reference to this part of ISO 527, including the type of specimen and the test speed, written in the following format:

Tensile test	ISO 527-3/1B/50
Type of specimen	_____
Test speed in millimetres per minute	_____

- b) to q) see ISO 527-1, clause 12, b) to q).

WITHDRAWN

DIN 53 381 Part 2

Testing of plastics

Determination of thermostability of polyvinyl chloride (PVC); discoloration method

Replacement for issue 09.75

1 Area of application and purpose

Testing in accordance with this Standard is used to assess the thermostability of PVC (including chlorinated PVC) in the form of polymers, moulding compounds and moulded materials at higher temperatures, at which colourless PVC discolours via yellow and brown to black.

It is suitable for monitoring the production and processing, for the acceptance, for the characterization and for comparison of PVC products and for trying out the effectiveness of thermal stabilizers¹ in moulded PVC materials.

As opposed to the dehydrochlorination method defined in DIN 53381 Part 1, only colourless, white or light-coloured moulded materials in the form of films or sheets can be tested in accordance with the discoloration method.

If polymers are to be assessed, it is necessary to use them to form moulding compounds in accordance with a defined formulation and to form films from the latter under exactly defined conditions.

The assessment of moulding compounds likewise requires films produced from them.

2 Brief description of the method

In order to assess thermostability in accordance with the method specified in this Standard, the discoloration of the test pieces, subjected to the effects of heat at temperatures above 125°C for a limited time, is assessed visually. Quantitative statements are made by means of comparison with agreed comparison scales or by a photometric route, for example in accordance with DIN 53236.

Note: The thermal decomposition of PVC is a complex reaction which is substantially affected by the type and content of thermal stabilizers¹ and other additives and by the gaseous medium. The decomposition can be detected by means of discoloration and the separation of hydrogen chloride (HCl).

Continued on pages 2 to 9

¹ For terminology, see DIN 50 035 Part 2

Standards Committee on Plastics (FNK) in DIN, the German Institute for Standardization
Standards Committee on Materials Testing (NMP) in DIN

2.1 Method D (oil bath test)

About 15 min. after test tubes half-filled with paraffin oil have been introduced into the temperature-controlled bath set to the testing temperature, a test piece is submerged in the oil as simultaneously as possible in each test tube and thus subjected to the action of atmospheric oxygen under heat. After defined time intervals, in each case a test tube is removed from the temperature-controlled bath. The test piece is then removed from the test tube and cooled down in air to room temperature, 18 to 28°C, in accordance with DIN 50 014.

2.2 Method E (oven test)

The test pieces are placed into the hot cabinet, set to the testing temperature, on racks which rotate during the test, and thus subjected to the action of atmospheric oxygen under heat. After defined time intervals, in each case a test piece is removed from the hot cabinet and cooled down in air to room temperature 18 to 28°C, according to DIN 50 014.

2.3 Method F (stabilimeter test)

The test piece in the form of a strip is fixed to the supporting plate and the latter is introduced into the slot-like channel of the metal block oven set to the testing temperature. By means of a mechanical apparatus, the supporting plate with the test piece is automatically withdrawn from the oven continuously during 1 to 2 hours, and thus the test piece is partially subjected to the action of heat.

3 Designation of the method

Designation of the determination of the thermostability of PVC when using method E:

<u>Thermostability</u>	<u>DIN 53 381</u>	-	<u>PVC</u>	-	<u>E</u>
Designation	DIN main number		Test material		Method

4 Equipment and testing materials

4.1 Method D

- Test tubes with an external diameter of 16 mm to DIN 12 395
- Paraffin oil (liquid paraffin)
- Temperature-controlled bath for temperatures up to $(200 \pm 1)^\circ\text{C}$
- Apparatus by means of which a number of test tubes can be kept immersed at least 70 mm in the bath liquid, and a heat shield, for example a plate, having holes for the test tubes
- 600 ml beaker, for example beaker to DIN 12 332 NF 600
- Wire mesh
- Weight with a mass of 1 kg
- Stopclock

4.2 Method E

- Hot cabinet of rectangular design with natural through-ventilation to DIN 50 011 Part 1, with
 - a usable volume of about 40 l,
 - a viewing window in the door,
 - internal lighting,
 - a heating output of 1.3 kW,
- 6 motor-driven and free-swinging suspended racks rotating at a rotational speed of about 4 min^{-1} during operation and having the dimensions 350 mm x 70 mm x 20 mm.

A glass thermometer (angled 90°) with a scale from 140 to 200°C is let into the front face of the racks. In the rear face of the racks there is a stop plate for the test piece supports. The racks are numbered.

Between the door of the cabinet and the interior there is a heat shield with a horizontal slot about 35 mm wide for the removal of the test pieces.

The temperature in the usable volume must not deviate by more than $\pm 0.5^\circ\text{C}$ from the set value in the range from 150 to 200°C . Here, the use of an electric 2-point controller with adjustable PID feedback and a resistance thermometer for air temperature measurements in the useful volume of the hot cabinet is recommended.

- Aluminium plates with a thickness of 0.9 mm.
Their dimensions must correspond to those of the racks.
- Stopclock

4.3 Method F

- Stabilimeter, for example of the following design:

The oven of the stabilimeter comprises a thermally insulated, electrically heated aluminium block, in which there is a horizontal channel with a rectangular cross section having a length of at least 200 mm to accommodate the supporting plate with the test piece.

The temperature in the channel must not deviate by more than $\pm 0.5^{\circ}\text{C}$ from the set value.

The rear end of the oven channel is connected to a gassing line, through which a gas flows.

Air or nitrogen is used as the gaseous medium and to remove the gaseous decomposition products separated during the thermal decomposition of the PVC. The gas stream (hydrogen chloride, plasticizer vapours and others) is set by means of a flow meter and kept constant by a gas volume flow controller.

- Supporting plate made of stainless steel with a thickness of about 0.4 mm.

The dimensions must correspond to those of the oven channel.

The upper side of the supporting plate is coated with polytetrafluoroethylene (PTFE).

- Drive motor to draw the supporting plate with the test piece out of the oven at a constant speed between 2 and 8 mm/min.

In order to take account of the time for the supporting plate with the test piece to heat up, a time relay may be switched on before the drive motor. After the start button has been pressed, in this case the drive motor switches on only after the set waiting time.

5 Production, shape and number of test pieces

5.1 Production

For the testing of a polymer or comparative tests on various polymers, thermal stabilizers or other additives, the average sample according to DIN 53 242 Part 1 to Part 3 is mixed with the other constituents of the formulation under the agreed conditions to form a moulding compound.

If the moulding compound is in powder form, then it is rolled, at a temperature of the mixing rolling unit to be agreed and for the mixing period, to form a film with a thickness of (1.0 ± 0.1) mm.

If the moulding compound is liquid, then it is gelled in a mould in a hot cabinet with positive through-ventilation according to DIN 50011 Part 1 at a temperature to be agreed and for a period to be agreed to form a film with a thickness of (1.0 ± 0.1) mm.

The production conditions must also be defined exactly for the testing of moulded materials. The thickness of test pieces taken from mouldings and semifinished products can differ from 1 mm.

5.2 Shape

The test pieces have the following dimensions:

- Method D: 40 mm x 6 mm x 1 mm
- Method E: 15 mm x 15 mm x 1 mm
- Method F: 250 mm x 15 mm x 1 mm

5.3 Number

The number of test pieces for testing according to methods D and E depends on the duration of the testing and is to be agreed.

Only one test piece is needed for testing according to method F.

6 Performance

6.1 Method D

The temperature control liquid in the temperature-controlled bath is heated to the testing temperature, preferably $(180 \pm 0.1)^\circ\text{C}$. If it is not defined in the technical conditions of supply for the product to be tested, the testing temperature must be agreed and specified in the test report.

The test tubes are filled to a height of about 60 mm with fresh paraffin oil and immersed at least 70 mm deep in the temperature control liquid. The number of test tubes and therefore also the number of test pieces is given by the duration of the test in minutes, divided by 5, increased by 1.

About 15 min. after the introduction of the test tubes into the temperaturecontrolled bath, a test piece is submerged in the paraffin oil in each test tube - as simultaneously as possible - and the stopclock is started.

As a rule, after times of 5 min. in each case, a test tube is removed from the temperature-controlled bath and emptied over the opening of a beaker provided with a wire mesh. The hot test piece is removed from the wire mesh, placed on a flat substrate and cooled down to room temperature, 18 to 28°C according to DIN 50014. In order to smooth the test piece, it is loaded for about 1 min. with the 1 kg weight.

Note: In order to reduce the number of test pieces for testing PVC with high thermostability, it is recommended either to choose a higher testing temperature or in each case to remove a test piece from the temperaturecontrolled bath after longer times, for example 10 or 15 min.

The time of the entire storage period is to be chosen such that the last test pieces to be removed from the temperature-controlled bath are black.

An untested test piece and, beside it, the test pieces that have been tested and freed of paraffin oil by wiping with cellulose are fixed to white board in the order in which they were removed from the temperature-controlled bath. Here, it must be ensured that the type of fixing does not affect the test pieces. For each test piece, the time in minutes for

which it was subjected to the testing temperature is recorded. This testpiece scale must be protected against the action of light.

6.2 Method E

The hot cabinet is set to the testing temperature, preferably $(180 \pm 0.5)^\circ\text{C}$. If it is not defined in the technical conditions of supply for the product to be tested, the testing temperature must be agreed and specified in the test report.

The number of test pieces is given by the duration of the test in minutes, divided by 5, increased by 1.

At most 6 test pieces are placed on each of the 6 aluminium plates in such a way that there is between them a spacing of at least 10 mm and a spacing of at least 14 mm from the outer edges of the plates.

The 6 aluminium plates with the test pieces are placed as quickly as possible on the 6 racks in the hot cabinet, so that the door needs to be opened only as briefly as possible. The door is then closed, the rack rotary drive and the stopclock are started. After time intervals of 10 or 15 min. in each case, which are to be agreed, after the rack rotary drive has been switched off, a test piece is removed from the hot cabinet and cooled down to room temperature of 18 to 28°C according to DIN 50 014. Here, too, in the same way as during the introduction of the aluminium plates with the testpieces, the door of the hot cabinet must be opened only briefly. The time for the entire storage should be chosen such that the last test pieces to be removed from the hot cabinet are black.

The test pieces are fixed to white board, as described in Section 6.1.

Note: If test pieces from a number of, for example 6, different PVC moulded materials are to be tested, it is recommended in each case to place 6 test pieces from the 6 different PVC moulded materials on the 6 aluminium plates and then to introduce these into the hot cabinet, which is set to the agreed testing temperature. After the agreed times, in each case an aluminium plate with the 6 test pieces from the 6 different PVC moulded materials is removed from the hot cabinet. This procedure is also recommended for test pieces which stick to the aluminium plate.

6.3 Method F

The oven of the stabilimeter is set to the testing temperature, preferably $(180 \pm 0.5)^\circ\text{C}$, and the gas volume flow is set to 0.5 l/min., for example. If they are not defined in the technical conditions of supply for the product to be tested, the testing temperature and the gas used must be agreed and specified in the test report. The sample strip is placed on the supporting plate. The sample strip is then fixed to the front end of the supporting plate by means of the clamp. The supporting plate with the sample strip is then pushed into the oven channel as far as the stop and the start button is pressed

immediately. After the expiry of the waiting time, for example 3 min., set α the time relay to heat up the supporting plate and the sample strip, the advance motor is switched on and draws the supporting plate with the sample strip out of the oven channel at the set speed, for example of 2 mm/min.

After the test has been completed, the sample strip is fixed to a white board provided with a time scale in min. The time scale corresponds to the set advance speed of the supporting plate, for example in the case of 2 mm/min. the scale distance between each minute is 2 mm.

Note: If the sample strips should shrink to a great extent in the oven, preceding annealing of the strips on filter paper for about 5 min. at 170 to 180°C in a hot cabinet is recommended.

7 Test report

In the test report, the following must be specified with reference to this Standard:

- a) Type and designation of the PVC polymer, the moulding compound or the moulded material
- b) Composition of the mixture and production of the test pieces
- c) Testing method used
- d) Testing temperature
- e) When method F is used: gas used, heating time and advance speed of the supporting plate with the sample strip
- f) Time between the removal of the test pieces when method D or E is used
- g) Time from the start of the hot storage until the first discoloration of the test piece
- h) Time from the start of the hot storage until the complete blackening of the test piece
- i) If appropriate, evaluation in accordance with an agreed comparison colour scale or in accordance with an agreed photometric method, specifying the means of measurement
- j) Agreed conditions deviating from this Standard
- k) Test date.

Standards cited

DIN 12 332	Glass laboratory equipment; low-form beakers
DIN 12 395	Laboratory equipment; test tubes
DIN 50 011 Part 1	Testing materials, components and equipment; hot cabinets, terminology, requirements
DIN 50 014	Atmospheric conditions and their technical application; standard atmospheric conditions

- DIN 50 035 Part 2** Terminology in the area of the ageing of materials; highly polymerized materials
- DIN 53 236** Testing of colorants; measurement and evaluation conditions for determining colour differences in paints, similar coatings and plastics
- DIN 53 242 Part 1** Raw materials for paints; sampling, terminology, general rules
- DIN 53 242 Part 2** Raw materials for paints; sampling, liquids
- DIN 53 242 Part 3** Raw materials for paints; sampling, highly viscous materials
- DIN 53 381 Part 1** Testing of plastics; determination of thermostability of polyvinyl chloride (PVC); dehydrochlorination method

Earlier issues

DIN 53 381 Part 2: 12.62; 09.75

Changes

As compared with the issue dated September 1975, the following changes have been made:

- a) Method D adapted to further testing development.
- b) Method E (oven test) and method F (stabilimeter test) newly incorporated

Explanations

The Standard, which was drawn up by subcommittee 1032 "Behaviour with respect to environmental influences", contains the new version of the issue dated September 1975.

Method D, what is known as the oil bath test, is very similar to Method I in the issue dated September 1975. It has already been used for decades for the production control of VC polymers.

Method E, what is known as the oven test, is used most frequently and replaces Method II in the abovementioned issue. Hitherto, no sufficient comparability between the test results could be achieved in this method. The reason for this is the inadequate constancy of temperature in terms of location and time of the hot cabinets (simple "drying cabinets" for chemical analysis purposes) used for this test. More than 10 years ago, the hot cabinet with rotating racks was developed for Method E and has also been proven worthwhile in practice. Owing to the rotation of the racks carrying the test pieces in the hot cabinet, the unavoidable local temperature differences are balanced out for the test. The racks, having a mass of about 6.7 kg, increase the heat capacity of the hot cabinet and thus reduce an excessively large decrease in the temperature during the introduction and removal of the test pieces, as does the heat shield between the

door and the usable volume. By means of these improvements in testing technology, sufficient comparability between the results is now achieved.

Method F, what is known as the stabilimeter test, has been used since about 1970. The design of this type of equipment makes it possible to draw test strips automatically and, above all, continuously from the action of heat and, in this way, to reduce the scatter of the test results⁴. A further advantage of the stabilimeter over the hot cabinet is that, apart from air, it is also possible to arrange for nitrogen to flow over the test pieces. For the testing of PVC moulding compounds which are processed with the unimpeded entry of air, for example the calendaring of films and coating with PVC pastes, air can be used as the test atmosphere.

The six tests (A to F) of thermostability described in the two parts of the Standard are based on two phenomena produced by the action of heat:

- separation of HCl and
- discoloration of the moulding compound.

Over the course of time, three methods of determination have been developed for each of the two phenomena. Within the next 5 years - until the Standard is revised - it is intended to test which of the methods of determination can be omitted. We request the relevant and interested users of the Standard to make their submissions to the Standards Committee on Plastics (FNK) in the DIN, Burggrafstraße 4 - 10, 1000 Berlin 30.

International patent classification

G 01 N 33/44

⁴ M. Boysen, Kunststoffe [Plastics] Vol. 65 (1975), pp. 293 - 295

DIN VDE 0472 Part 614

Testing of cables, wires and flexible cords
Thermal stability

This Standard, also approved by the Chairman of the Verband Deutscher Elektrotechniker [Association of German Electrical Engineers] (VDE) is therefore simultaneously a VDE regulation in the sense of VDE 0022. It has been included in the VDE Regulations under the above number and publicised in etz, the electrical engineering journal.

Copying - even for in-house purposes - is not permitted.

Testing of cables, wires and flexible cords;
Thermal stability

Partial replacement for
VDE 0472/09.71 and
VDE 0472 d/12.77
but see the
changeover deadline!

This Standard corresponds to the harmonization document 385, Section 17, of CENELEC, the European Committee for Electrical Engineering Standardization; identical to IEC 540 (1982), Section 17.

This Standard contains the test methods which must be applied in accordance with the Standards for cables, wires and flexible cords in order to determine properties.

The content of the Standard was published in the draft DIN 57472 Part 614/VDE 0472 Part 614/03.84

Commencement of validity

This Standard (VDE regulation) applies from 1 November 1985.

In addition, DIN VDE 0472/09.71 and VDE 0472 d/12.77 continue to apply in those Standards in which they are cited.

Continued on page 2

1 Area of application

This Standard applies to the testing of the thermal stability of insulating sheaths and covers of cables, wires and flexible cords.

2 Testing equipment and testing materials

- 2.1** Glass tube, fused shut at one end, 110 mm long, of about 5 mm diameter and with a clear width of (4.0 ± 0.5) mm.
- 2.2** Universal indicator paper.
- 2.3** Temperature-controlled enclosure for a temperature of $(200 \pm 0.5)^{\circ}\text{C}$.
- 2.4** Anschütz thermometer to DIN 12777, scale value 0.2°C , error limit $G = 0.4^{\circ}\text{C}$.
- 2.5** Time measuring device, for example stopclock.

3 General

DIN VDE 0472 Part 1 applies, if no different definitions are made in this Standard.

4 Samples

Three sample pieces each having a mass of (50 ± 5) mg are taken from the test piece, cut into one or a number of strips and each introduced into a glass tube according to Section 2.1. A level of 30 mm must not be exceeded.

5 Preparation of the test

A longitudinally folded strip about 3 mm wide of dry universal indicator paper according to Section 2.2 of about 20 mm length is pushed into the opening in the glass tube such that around 10 mm of the strip projects beyond the edge of the glass tube. In order to hold it, the indicator strip is bent over.

6 Performance

The prepared glass tubes are introduced into the temperaturecontrolled enclosure according to Section 2.3, which has already been heated to the testing temperature of $(200 \pm 0.5)^{\circ}\text{C}$, and the time measuring device according to Section 2.5 is started.

The immersion depth of the glass tubes is to be about 60 mm. The timeperiod until the first visible red coloration of the universal indicator paper, corresponding to pH 3, is registered. In order to detect the changeover point more clearly, the universal indicator paper should be renewed about 10 minutes before the defined or to be expected changeover point.

7 Evaluation

The test is deemed to have been passed if the average of the thermal stability, determined from the results of the three samples, does not fall below the value defined in the Standards for cables, wires and flexible cords.

Standards cited

DIN VDE 0472 Part 1	Testing of cables, wires and flexible cords; general
DIN 1277	Laboratory equipment made of glass; Anschütz thermometer set
HD 385	Test methods for insulations and sheaths of electric cables and cords (elastomeric and thermoplastic compounds)
identical to	
IEC 540 (1982)	

Earlier issues

VDE 0472:	01.51	
VDE 0472:	11.54x	
VDE 0472:	06.65	┐
VDE 0472a:	03.69	
VDE 0472b:	12.69	
VDE 0472c:	09.71	└
VDE 0472d:	12.77	

Printed together as VDE 0472/09.71

Changes

As compared with VDE 0472/09.71 and VDE 0472 d/12.77, the following changes have been made:

- Test method revised, in particular also from an editorial point of view.
- Contents divided up into the Standards of the DIN VDE 0472 series, corresponding to the previous paragraph numbering.

Explanations

This Standard was drawn up by committee 411 "High-power cables and insulated high-power cords", by committee 412 "Telecommunications cables and wires" and working group 411/412.0.1 "Tests on cables, wires and flexible cords" of the German Electrical Engineering Commission in DIN and VDE (DKE).

International patent classification

G 01 N 1/04

G 01 N 25/00

H 01 B 7/00

H 01 B 9/00

H 01 B 11/00

DIN 53 447**Testing of plastics****Determination of stiffness in torsion as a function of temperature**

Relationship to a draft ISO/DIS 458.2 issued by the International Organization for Standardization (ISO): see Explanations

1 Purpose and area of application

Testing in accordance with this Standard is used to determine the stiffness in torsion of plastics as a measure of their stiffness over a wide temperature range, in particular of soft plastics (for example polyvinyl chloride containing plasticizer (soft PVC)) below 0°C. In addition, the temperature at which the test piece has a selected stiffness in torsion can therefore be determined for material monitoring or development.

2 Reference standards

DIN 50 014 Atmospheric conditions and their technical application; standard atmospheric conditions

3 Terminology

The stiffness in torsion T according to this Standard is the ratio of the shear stress, kept constant during the test, and the displacement (angular deformation) caused thereby after a loading time of 5 s.

4 Designation of the method

Designation of the method for determining the stiffness in torsion as a function of the temperature (T)

Stiffness in torsion to DIN 53447 - T

Continuation on pages 3 to 7
Explanations page 8

5 Testing instrument

5.1 Stiffness-in-torsion testing instrument which allows a torque to be applied to the test piece over the free clamped length (measuring length), which is around 40 mm, in order to achieve a torsion angle between 50 and 60°. It must be possible to read the torsion angle to $\pm 0.5^\circ$. Figure 1 shows the principle of the testing instrument.

Note: The test piece is clamped in between the lower, nonrotatable and upper, rotatable clamping device. By means of the two pans with weights suspended on cords, a specific torque is exerted on the test piece via the deflection rollers and the rotary disc. The lockable rotary disc is provided with a scale with angular divisions, on which the torsion angle can be read off. In newer designs of the testing instrument, the docking device is automatically fixed again by means of a timer and an electromagnet 5 s after being released in order to reduce measurement errors.

For testing at temperatures below 0°C it is recommended to heat the shaft bearing of the rotatable clamping device in order to prevent additional bearing friction.

5.2 Various weights (for example lead shot) in order to change the torque in accordance with the stiffness of the test piece in such a way that a torsion angle of 50 to 60° according to Section 9.4 is achieved.

5.3 As a temperature control vessel for the clamped test piece, either a Dewar vessel of suitable dimensions having a stirrer or a corresponding liquid thermostat can be used. Uniform temperature control of the test piece to any temperature in the desired temperature range (for example -70 to 100°C) by means of a liquid must be possible. It must be possible to maintain the temperature on the test piece to 1 K.

Note: The temperature control liquid must remain highly fluid within the desired temperature range. Care must be taken that the test piece is neither caused to swell nor attacked in any other way by the liquid. Recommended liquids are: ethyl alcohol, butanol, hexane, silicone oil or a mixture of 87 parts by volume of trimethyl phosphor and 13 parts by volume of water. For temperatures down to -70°C, a mixture of 50 parts by volume of ethyl alcohol, 30 parts by volume of ethylene glycol and 20 parts by volume of water has been tried and tested.

For the purpose of cooling, solid carbon dioxide and, for the purpose of heating, an immersion heater of which the heating output can be adjusted can be used.

5.4 Temperature measuring instrument which allows the temperature of the temperature control liquid to be measured to ± 0.5 K as close as possible to the test piece.

5.5 Dial gauge having a scale division of 0.01 mm, for example to DIN 878, for measuring the thickness and width of the test pieces. In the case of soft plastics, the measuring pressure should lie between 0.01 and 0.03 N/mm²

5.6 Timer which can be read to 0.1 s.

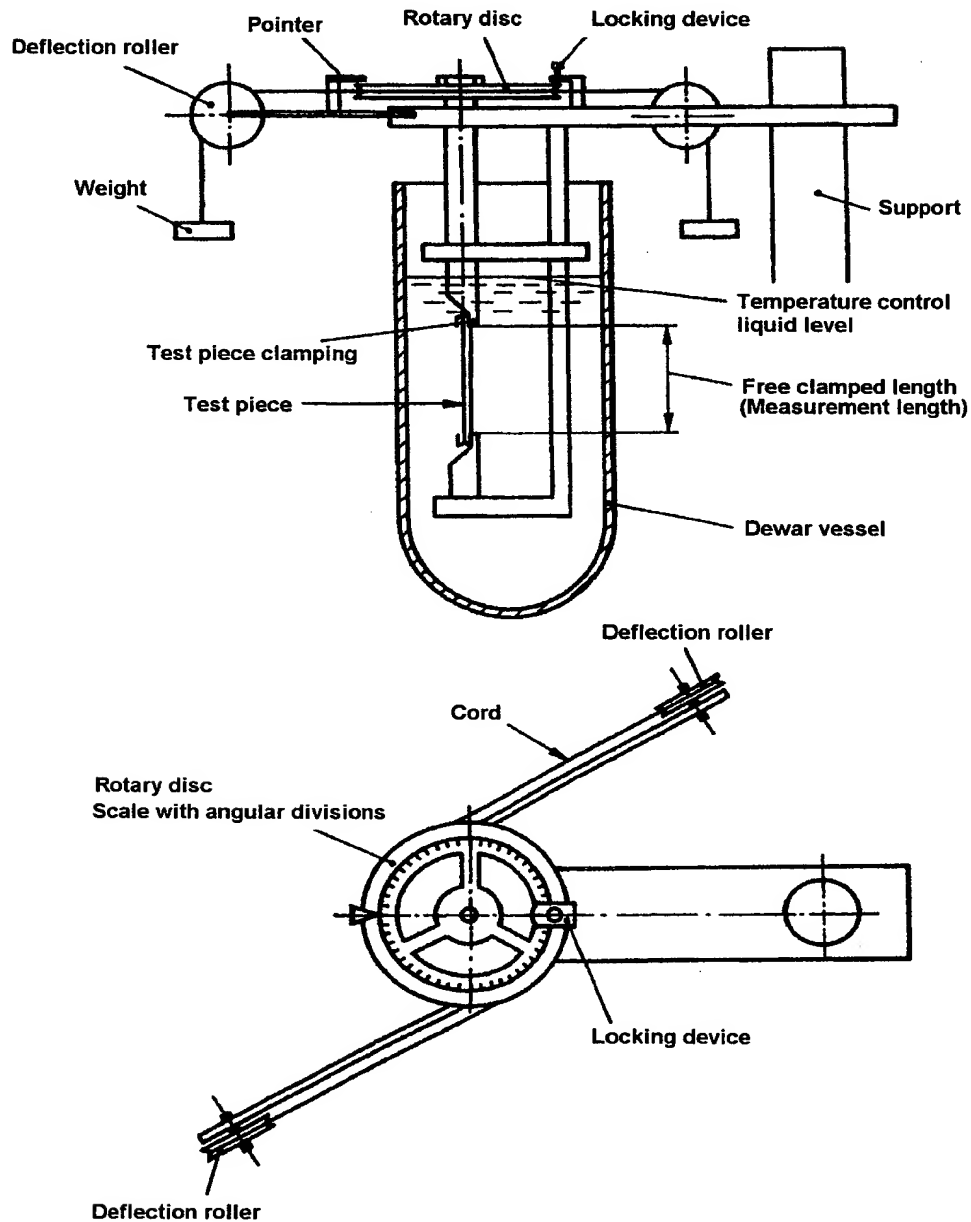


Figure 1. Principle of the stiffness-in-torsion testing instrument

6 Production and shape of the test piece

From the product to be tested, rod-like test pieces of 60 to 65 mm length, 6.0 to 6.3 mm width and 1 to 5 mm, preferably 3 mm, thickness are produced by shaping suitable for the material, for example cutting, punching, milling. The thickness range 1 to 5 mm makes it possible to test moulding materials of different stiffness. The edges of the test pieces must have no burrs. The test pieces are each provided with a hole on their broad side in the vicinity of their two ends, in order to be able to fix them in the lower and upper clamping device of the testing instrument by using screws. The diameter and the spacing of the holes depend on the geometry of the clamping device.

7 Number of test pieces

2 test pieces are tested. In the case of anisotropic products, 2 test pieces each are tested in each main direction.

8 Pre-treatment of the test pieces

The test pieces are stored for at least 48 h in the standard climate according to DIN 50 014 - 23/50 - 2.

9 Performance

9.1 Before the test, at at least 3 points of the test piece within the free clamped length (measurement length), the width must be measured $b \pm 0.1$ mm and the thickness to ± 0.01 mm. Test pieces in which the largest and smallest thickness values differ by more than 3% are not tested.

9.2 The rotary disc with angular scale is locked at 0° and the test piece is clamped into the upper and lower clamps at room temperature such that its longitudinal axis coincides with the axis of rotation of the rotary disc. For this purpose, shims can be used on the two clamps. The free clamped length (measurement length) of the test piece is measured to 0.5 mm.

Note: if measurements are carried out with the clamped test piece over a relatively large temperature range, it expands noticeably or contracts. As a result, the test results are afflicted by additional errors. In order to avoid these errors, a relatively simple modification of the lower clamping device in accordance with Figure 2 is worth recommending.

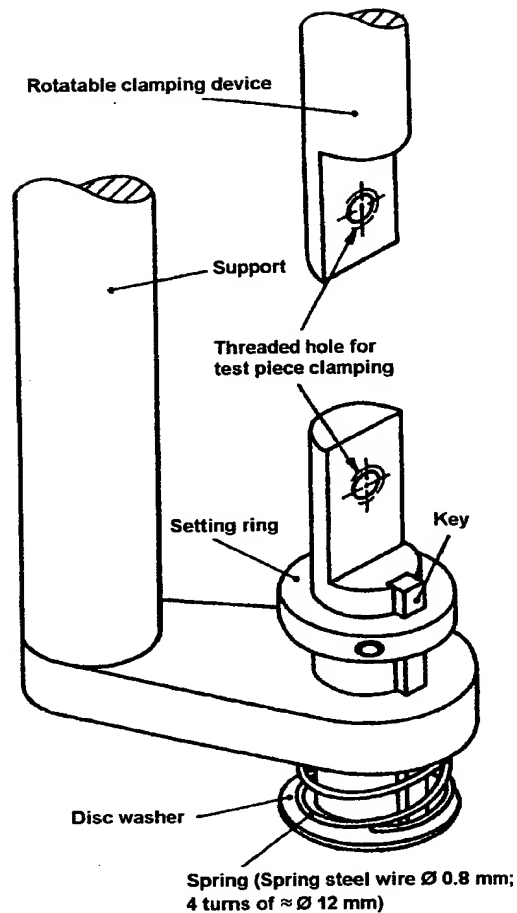


Figure 2. Modified lower clamping device of the stiffness-in-torsion testing instrument

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9.3 The clamped test piece has its temperature controlled for 5 min in the temperature control liquid brought to the lowest testing temperature (of the desired temperature range).

9.4 The torque is exerted on the test piece by means of weights distributed uniformly to both pans after the locking has been released. In order to avoid over-twisting the test piece, the torque should be transmitted without shocks within about 1 s. 5.0 s after the locking has been released, the rotary disc is locked again and the torsion angle is read off. The weights should be chosen such that the torsion angle is 50 to 60°. After the torsion angle has been read off, the rotary disc must immediately be rotated back into the 0° position and locked.

Note: It is advantageous to determine the weights necessary to achieve a torsion angle of 50 to 60° after 5 s loading on separate test pieces and, if appropriate, the necessary test piece thickness by means of prior tests.

9.5 For the testing at the next, higher temperature, the procedure as described in Sections 9.3 and 9.4 must be followed. In order to reduce the applied torque, weights of lower mass must be used in order to achieve a torsion angle of 50 to 60° after 5 s. The stiffness in torsion T in N/mm² is calculated in accordance with the following numerical equation:

$$T = \frac{57.3 \cdot 16 \cdot l \cdot M}{b \cdot h^3 \cdot u \cdot \varphi}$$

Here:

- M is the torque in N · mm
- l is the measurement length of the test piece in mm
- b is the average width of the test piece in mm
- h is the average thickness of the test piece in mm
- φ is the torsion angle in degrees
- u is the factor according to the table
- 57.3 is the conversion factor from angles to radians ($180^\circ / \pi$)

Note: The factor u is calculated in accordance with the following equation:

$$u = 5.33 - 3.36 \frac{h}{b} \left(1 - \frac{h^4}{12 \cdot b^4} \right)$$

The stiffness in torsion of each test piece is plotted as a function of the testing temperature in a graph with logarithmic ordinate and linear abscissa.

Note: From this graph, the stiffness-in-torsion temperatures, for example, which are important for the characterization of PVC moulding compounds containing plasticizer can be determined by interpolation for $T = 310$ N/mm², $T = 23$ N/mm² and $T = 4$ N/mm².

Factor u as a function of the ratio b/h

b/h	u	b/h	u
1.20	2.64	3.00	4.21
1.30	2.82	3.05	4.23
1.40	2.98	3.10	4.25
1.50	3.13	3.15	4.26
1.60	3.26	3.20	4.28
1.70	3.37	3.25	4.30
1.80	3.48	3.30	4.31
1.90	3.57	3.35	4.33
2.00	3.66	3.50	4.37
2.25	3.84	4.00	4.49
2.50	3.99	4.50	4.58
2.75	4.11	5.00	4.66
2.85	4.15	5.50	4.72
2.90	4.17	6.00	4.77
2.95	4.19	6.50	4.81

10 Evaluation

The torque M in $\text{N} \cdot \text{mm}$ exerted during the testing is calculated in accordance with the following equation:

$$M = r \cdot g \cdot m$$

Here:

r is the effective radius in mm, calculated in accordance with the equation

$$r = \frac{(d_1 + d_2)}{2}$$

where

d_1 is the diameter of the rotary disc in mm (measured in the guide groove of the cord to 0.1 mm)

d_2 is the diameter of the cord in mm to 0.1 mm

g is the acceleration due to gravity ($g = 9.807 \text{ m/s}^2$)

m is the sum of the masses of the weights and of the two pans in kg (to ± 1 in the third significant figure)

11. Test report

In the test report, the following must be specified with reference to this Standard:

- a) Type, form supplied and identification of the product
- b) Test piece dimensions in mm
- c) Treatment of the test pieces
- d) Temperature control liquid
- e) Free clamped length (measurement length) in mm
- f) Table of test results (torsion angle, stiffness in torsion and testing temperature)
- g) Graph with logarithm of the stiffness in torsion as a function of the temperature
- h) Conditions deviating from this Standard
- i) Test date.

Explanations

The present Standard was drawn up by subcommittee 102.1 "Mechanical and thermal properties". The Standard is based on the ISO/TC 61 Draft International Standard ISO/DIS 458.2 - 1980 "Plastics - Determination of stiffness in torsion of flexible materials (Revision of ISO/R 458-1965) - Plastics; Determination of the stiffness in torsion on flexible materials".

The term "stiffness in torsion" in the sense of this Standard identifies a material property, while the term stiffness in torsion (product of shear modulus and torsional resistance) also includes the cross-sectional dimensions of the torsion rod (see DIN 13 316).

It must be noted that the results obtained when determining the stiffness in torsion in accordance with this method are not independent of the test piece dimensions.

This Standard is based on the following prior studies:

R.F.Clash, jr and R.M. Berg, Stiffness and Brittleness of Nonrigid VinylChloride-Acetate Resin Compounds, Modern Plastics, Vol. 31 (July 1944)

USA Standard ANSI/ASTM D 1043-72.

WITHDRAWN

DIN 53 372

Testing of plastics films

Determination of break at low temperature of films of non-rigid polyvinyl chloride

1. Purpose

Testing in accordance with this Standard is used to determine the fracture (break) at low temperature according to Section 2 of films of non-rigid polyvinyl chloride (PVC) up to a maximum of 0.5 mm thickness and PVC foam films up to 2 mm thickness.

This temperature value has only an orienting character and is intended to permit comparisons, for example between a number of products, with regard to the fracture behaviour at low temperature. The test results according to this Standard cannot readily be transferred to any desired application forms and conditions because of the multifarious nature of the types of stress which occur in practice.

2. Terminology

The low-temperature fracture temperature according to this Standard is the average temperature of a temperature range. The temperature range begins at the temperature at which no sample has yet fractured or been damaged under the conditions according to this Standard, and ends at the temperature at which all the samples have fractured or been damaged.

3. Brief description of the method

At fixed testing temperatures, a determination is carried out as to how many of a fixed number of samples bent into loops are damaged or fractured by a defined, rapid bending stress. Samples which either have begun to break at the side or in which the formation of a notch at the fold in the bent state is to be observed by means of viewing with a magnifying glass with 6-fold magnification count as damaged. Samples exhibiting white fracture at the bending point do not count as damaged; however, the testing temperature from which white fracture occurs must be specified in the test report. The low-temperature fracture temperature is determined by means of graphical evaluation.

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4. Removal and form of the samples

Samples $60 \text{ mm} \pm 1 \text{ mm}$ long \times $15 \text{ mm} \pm 0.1 \text{ mm}$ wide are taken longitudinally - distributed as uniformly as possible over the web width - and, if appropriate, also transversely from wide film webs. Samples with visible faults which come into the loop curvature are not tested.

Note: The surface condition (for example graining¹) achieved by means of embossing the film does not count as a visible fault. In the case of such films, the measured results depend on how deeply the surface is embossed.

The longitudinal edges of the samples must be cut with a cutting implement which ensures smooth cut edges. Samples are taken transversely from film tubes only if the tube width between the tube edges is $> 60 \text{ mm}$. The same is true in the same sense for narrow strips.

5. Number of samples

At each testing temperature according to Section 8.2, 6 samples are tested. In arbitration cases, 12 samples are tested at each testing temperature, if not otherwise agreed.

6. Pre-treatment of the samples

If not otherwise agreed, the samples are stored for 24 hours under the standard conditions 23/50 of DIN 50 014², in arbitration cases to constant weight.

7. Testing instrument

7.1. Testing machine

The testing machine comprises:

- a) A metal anvil (for example made of steel) having a flat surface with 6 flat clamping springs for clamping 6 samples. It must be ensured by means of marking lines (for example engraved lines) that the samples can always be clamped in the same position.
- b) 6 plungers (drop hammers) made of steel with flat end faces of 18 mm diameter and slightly rounded edges. The mass of a plunger must be 200 g. The plungers are held above the samples by means of pawls in a holder (for example a tripod which is connected firmly to the anvil) such that the edge of the loop lies under the centre of the plunger. The drop height, measured between the anvil and the end face of the plunger must be $200 \text{ mm} \pm 1 \text{ mm}$. The pawls must permit the plungers to be released without delay.

¹ For the term graining, see DIN 51 964

² A deviation of the relative atmospheric humidity of $\pm 5\%$ instead of $\pm 3\%$ is permissible.

- c) A temperature measuring instrument (for example thermocouple or resistance thermometer) which permits the temperatures to be measured in the vicinity of the samples.

7.2. Equipment for producing the test atmospheric conditions

The equipment must permit dry atmospheric conditions to be produced down to at least -60°C , control of the temperature of the test chamber (see Section 7.3) by means of an air stream and maintenance of the temperature in the test chamber during the test.

7.3. Test chamber³

The test chamber must be constructed in such a way that it is able to accommodate the samples and the testing machine (but at least the anvil) and that the air stream (see Section 7.2) cools down the samples and the anvil to the testing temperature (see Section 8.2).

7.4. Film cutting implement

Any film or paper cutting implement with which the required width can be cut to ± 0.1 mm and the required length can be cut to ± 1 mm which produces a smooth cut edge free of notches can be used as the cutting implement

7.5. Thickness measuring instrument

to DIN 53 370

8. Performance

8.1. Measuring the thickness of the sample

Before the test, the thickness of the samples is in each case measured at the centre of the sample.

8.2. Testing temperature

As a rule, the testing is performed at the following temperatures:

20°C , 15°C , 10°C and so on, falling by 5 degrees.

A smaller gradation can however be agreed upon - particularly in arbitration cases (see Section 8.4).

8.3. Clamping the samples

The cut samples are bent to form a loop at room temperature (to DIN 50 014) and are pushed under the clamping springs fitted to the anvil. In this case, the intention is to form a loop curvature with about 3 mm radius. This can be monitored by using an

³ The test chamber can also be a testing room or an air-conditioned cabinet.

appropriate mandrel. As a rule, this loop curvature is established if the sample is pushed through as far as the marking line (see Section 7.1a).

8.4. Performing the measurement

After the 6 samples have been clamped in, the test chamber is closed. The plungers are located in the drawn-up position and are kept in this position by the pawls. The samples have their temperature controlled at the testing temperature t_1 for at least 5 minutes. The plungers are then released one after another and allowed to fall freely onto the loops. The plungers are then drawn up again, the test chamber is opened and a check is made as to how many of the 6 samples have been fractured or damaged by the stress. The number $n(t_1)$ is noted. 6 new samples are then clamped in, the testing is carried out at the testing temperature t_2 and the number $n(t_2)$ is noted. The testing is continued until all 6 samples are fractured or damaged at a temperature t_k , that is to say the number $n(t_k)$ is equal to the number n_0 of samples to be tested at each temperature.

Note: As a rule, it is not necessary to test the samples at all the testing temperatures. It is sufficient if a check is made between the testing temperatures at which $n(t_1) = 0$ and $n(t_k) = n_0$. The temperature range of interest can be determined approximately under certain circumstances by means of prior tests.

9. Evaluation

The values $n(t_k)$ obtained are plotted on graph paper with appropriate graduation (abscissa: temperature; ordinate: number of fractured or damaged samples). A straight line is then drawn such that it best passes through the points obtained. The temperature at which this straight line reaches the value $\frac{1}{2}n_0$ is the low-temperature fracture temperature according to this Standard.

10. Test report

In the test report, the following must be specified with reference to this Standard:

- Type, form supplied and identification of the film
- Surface condition (for example graining) of the film
- Production date of the samples
- Thickness of the samples
- Average
- Number of samples tested at each testing temperature
- Type and duration of the pre-treatment of the samples
- Low-temperature fracture temperature and evaluation graph
- Other observations during the test, for example white fracture
- Conditions deviating from this Standard
- Test date.

Explanations

The behaviour of films when stressed at low temperature is one of the most important properties. In round robin tests with an extremely wide range of types of film, it transpired that agreement between results could be obtained only on nonrigid PVC films; all the other films investigated resulted in measured values which were scattered to such an extent that it was initially necessary to give up the general introduction of the test method. The question as to whether the PVC film to be tested is a nonrigid PVC film in the sense of this Standard is decided at room temperature. If the shear modulus, measured in accordance with DIN 53445, is equal to or less than $5 \cdot 10^3 \text{ kp/cm}^2$, then this is a non-rigid PVC film. This value of the shear modulus corresponds to a modulus of elasticity in tension of about 12 000 to 15 000 kp/cm^2 .

If a number of non-rigid PVC films are to be compared with one another, it is necessary to take into account the fact that the low-temperature fracture temperature exhibits a certain dependence on the sample thickness. In general, the curve of the low temperature fracture temperature, plotted against the sample thickness, passes through a shallow maximum. Therefore, only films with an approximately equal thickness can be included in the strict comparison.

Finally, reference should also be made to an arithmetic evaluation of the test results in order to determine the low-temperature fracture temperature. This is an average value calculation which is performed in the following way: the respective number of samples fractured at a specific testing temperature is multiplied by the latter. The sum of all the fractured samples and of all the products formed (testing temperature times number of fractured samples) is calculated. The temperature at which all 6 samples are fractured should not be taken into account, since otherwise the result will be a low-temperature fracture temperature which is somewhat too low. Then, if the sum of all the products is divided by the sum of all the fractured samples, the result is the low-temperature fracture temperature.

The multiplication should begin at the testing temperature at which the first sample fractures. However, if the case occurs in which no sample is fractured at a specific testing temperature but then all the samples fracture at the next lowest temperature, then this type of evaluation can no longer be applied.